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COMBUSTION OF MIXTURES OF METAL SULFATES WITH MAGNESIUM OR ALUMINUM

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ABSTRACT: Data are presented on heat of combustion, critical particle size and rates of combustion of Mg and Al mixtures with various sulfates and hydrated sulfates. Mixtures with compounds not decomposing at melting temperature burn at rates independent of pressure, with combustion apparently taking place mainly in the condensed phase. The other group, decomposing at or below melting temperature, burn more rapidly as pressure rises, with combustion apparently taking place mainly in the gas phase.

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There is little data in the literature on combustion of mixtures of sulfates with magnesium or aluminum. It is known that some of them ignite upon heating [1], and that barium and calcium sulfates have been proposed as oxidizers in pyrotechnic illuminating mixtures [2]. Anhydrous sulfates yield to nitrates as oxidizers, since they require considerably more heat for decomposition according to the scheme $Me_xSO_4 \rightarrow Me_xS + 2O_2$. The oxygen content of the sulfates is comparable with the oxygen content of the nitrates of the same metals.

Together with mixtures containing anhydrous sulfates, there has been interest in research on combustion of mixtures of magnesium (aluminum) with crystalline hydrates of the sulfates. Mixtures of these metals with water are capable of burning [3]. The water contents in such crystal hydrates as $Na_2SO_4 \cdot 10 H_2O$ and $MgSO_4 \cdot 7 H_2O$ is high (56 and 51 wt. % respectively), and the total oxygen content is considerably higher than in $NaNO_3$ (see table).

The combustion of stoichiometric mixtures of magnesium (aluminum) with anhydrous Li, Na, K, Mg, Ca, Ba, and Cu sulfates and the crystalline hydrates $Na_2SO_4 \cdot 10 H_2O$, $MgSO_4 \cdot 7 H_2O$ and $FeSO_4 \cdot 7 H_2O$ were studied. Magnesium (aluminum) powders had an activity of 99.6% (92.5%) and an average particle size of 35μ (1μ). Analytical grade reagent and chemically pure grades were used as oxidizers. The particle size of all oxidizers was less than 250μ .

Determination of the critical combustion diameter (d_{cr}) was carried out at $p = 1$ atm in air. The mixtures were placed in glass beakers, and the charge densities were $0.8-1.0\text{ g/cm}^3$ ($K_{pack} = 0.2-0.5$). The relationship of combustion rate to pressure was studied in a constant pressure bomb, in a nitrogen

atmosphere. Separate tests were carried out in argon, and they gave the same results as in nitrogen. The charges were grains ($K_{\text{pack}} = 0.8-0.9$), 15 mm in diameter, jacketed with a cellophane strip on the sides and solidly set into a glass tube. A 12.8/87.2 wt. % Mg/BaO₂ mixture was the igniter, which was initiated in turn with an electric coil. A photo recorder or movie camera was used for determination of combustion rate.

a Окислитель	Общее кислородное содержание, вес. % b	Генетика образования, ккал/моль c ΔH ₂₉₈	d Содержание Me в stoichiometрической смеси, вес. %		e Расчетная теплота горения в смеси, ккал/кг		f d _{cr} горения при p=1 атм, мм Mg +, - Al +, -	
			Mg	Al	Mg	Al	Mg +, -	Al +, -
Li ₂ SO ₄	58	343	47	36	1640	1620	4/2	7/4
Na ₂ SO ₄	45	331	40	33	1400	1360	4/2	7/4
K ₂ SO ₄	37	343	34	29	1230	1180	4/2	12/10
MgSO ₄	53	306	44	37	1620	1610	7/4	16/12
CaSO ₄	47	342	42	34	1500	1470	4/3	17/12
BaSO ₄	27	350	30	23	1000	910	5/3	17/12
CuSO ₄	40	184	38	31	1570	1560	7/4	10/7
Na ₂ SO ₄ ·10H ₂ O	70	1033	51	44	1620	1610	4,2	20/17
MgSO ₄ ·7H ₂ O	71	609	52	45	1670	1670	10/8	—/46
FeSO ₄ ·7H ₂ O	63	719	49	42	1630	1620	8/6	13/12
H ₂ O ₂ , g	89	68,4	57	50	1800	1810	12/10	32 28
NaNO ₃	56	112	42	35	2050	2030	3/2	—

Key: a. Oxidizer

b. Total oxygen content, wt. %

c. Heat of formation, ΔH₂₉₈, kcal/mole

d. Me content in stoichiometric mixture, wt. %

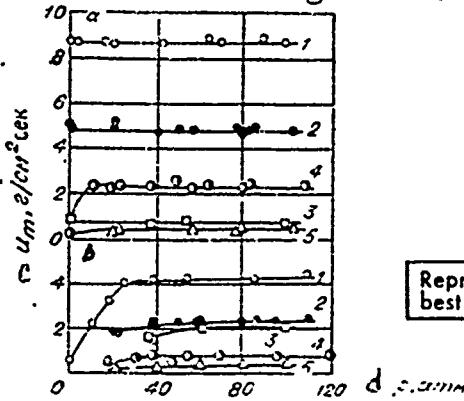
e. Calculated heat of combustion in mixture, kcal/kg

f. d_{cr} of combustion at p = 1 atm, mm

g. H₂O (l)

The smallest combustion d_{cr} were observed in mixtures of magnesium with Li₂SO₄, Na₂SO₄, K₂SO₄ and Na₂SO₄·10 H₂O. These mixtures had a d_{cr} which was almost the same as a stoichiometric mixture of magnesium with NaNO₃. Upon substitution of aluminum for magnesium, d_{cr} of the mixtures increased particularly sharply in the case of some crystalline hydrates (five times for Na₂SO₄·10 H₂O). Combustion of the mixtures of metals with crystalline hydrates was accompanied by scattering of the charge, and it proceeded less stably than in mixtures with anhydrous sulfates.

The combustion rates of mixtures of magnesium with Li_2SO_4 , Na_2SO_4 and K_2SO_4 remained constant over the pressure range of 1-100 atm (fig. 1a). In the mixture of magnesium with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, a rapid increase in combustion rate was observed from 1 to 10 atm; at higher pressures (up to 100 atm), the combustion rate was constant, but less than in mixtures with anhydrous Na_2SO_4 . A mixture of magnesium and water burned considerably slower than a mixture with the sulfates. Its combustion rate remained constant over the 20-100 atm pressure range. A change in packing coefficient of the mixtures of magnesium with Li_2SO_4 and Na_2SO_4 , from 0.6 to 0.9, had no effect on the combustion rate value. Tests carried out at pressures of 20 and 80 atm, using Na_2SO_4 , having particle sizes < 50 , 50-63 and 100-200 μ , showed that the particle size of this oxidizer has no effect on combustion rate. The combustion rates of mixtures of aluminum with the same oxidizers (see Fig. 1b) increased negligibly over the pressure range from 20 to 100 atm (in the case of K_2SO_4 , from 40 to 100 atm). They are more difficult to ignite, and they burn approximately three times slower than the corresponding mixtures with magnesium.



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Fig. 1. Combustion rate vs. pressure of mixtures of magnesium (a) and aluminum (b) with Li_2SO_4 (1), Na_2SO_4 (2), K_2SO_4 (3), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (4), and H_2O (5).

Key: c. U_p , $\text{g}/\text{cm}^2 \cdot \text{sec.}$
d. p , atm

The combustion rate of mixtures of magnesium or aluminum with Mg, Ca, Ba, and Cu sulfates and the crystalline hydrates $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ increased with increase in pressure (Fig. 2a, b). It is clear from the examples of MgSO_4 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ that, as in the case of Na_2SO_4 and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, the

presence of water of crystallization decreases the combustion rate of the mixture. Mixtures of aluminum with CuSO_4 and CaSO_4 burn somewhat more rapidly than mixtures of magnesium with the same oxidizers, at increased pressures.

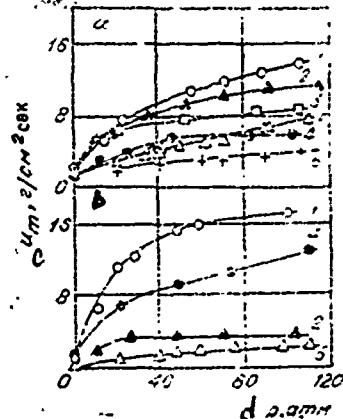


Fig. 2. Combustion rate vs. pressure of mixtures of magnesium (a) and aluminum (b) with CuSO_4 (1), BaSO_4 (2), MgSO_4 (3), CaSO_4 (4), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (5) and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (6).

Key: [c, d, same as in fig. 1.]

The oxidizers used can be divided into two groups, by the nature of the resulting function $U_t = f(p)$:

(1) Li_2SO_4 , Na_2SO_4 , K_2SO_4 , $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and H_2O , forming mixtures with magnesium, the combustion rates of which are independent of pressures; in the case of aluminum, the combustion rate increases negligibly over the 20-100 atm pressure range;

(2) MgSO_4 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, CuSO_4 , CaSO_4 , and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, in which their combustion rate with magnesium or aluminum increase with increase in pressure.

The fact that the sulfates of lithium, sodium and calcium melt without decomposing, at temperatures of 885, 860 and 1070°C, respectively, attracts attention. Apparently, oxidation of magnesium in burning of mixtures with these sulfates, proceeds predominantly in a melt of the oxidizer, i.e., in the condensed phase. It is possible that oxidation of magnesium takes place partially in the condensed phase and by its burning in a mixture with water. Increased pressures facilitate this. The lower oxidizing power of water vapors with respect to aluminum are caused by a sharper decrease in combustion rate of its mixtures with crystalline hydrates (compare Na_2SO_4 and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in mixtures with magnesium and aluminum) and a considerable increase in d_{cr} .

The sulfates of metals which decompose upon melting or below the melting temperature (CuSO_4) are in the second group.

Upon combustion of mixtures of these sulfates with magnesium (aluminum), a bright flame forms over the surface of the charge. The slag becomes porous and wrinkled. Apparently, combustion of the metal takes place in the smoke-gas phase, formed by the products of decomposition of the oxidizer. The use of the acid salt NaHSO_4 , decomposing at 320°C , in a mixture with magnesium, in place of Na_2SO_4 , led to an increase in rate with increase in pressure.

The differences in dependence of combustion rate on pressure of mixtures of magnesium and aluminum with the sulfates studied can be explained by oxidation of the metal in a melt of the sulfate or in the gaseous products of decomposition of the latter.

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